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Work on the contract # F49620-97-0029 was completed by 1/15/2000. During this reporting period, the research teams at the University of Houston and The Aerospace Corporation investigated the surface chemical interaction of a number of molecular adsorbates with the (100) face of titanium carbide and vanadium carbide using an array of surface analytical measurement tools. Adsorbates included oxygen and water, considered important from an environmental "aging" perspective, carbon monoxide and ammonia as probes of the electronic structure model developed within this program, and a series of alcohols including methanol, ethanol, trifluoroethanol, isopropanol, and methyl allyl alcohol as probes of interfacial reactivity. An array of surface analytical techniques producing independent yet complimentary data were employed to develop a complete chemical and structural picture of the adsorption and reaction of these molecular adsorbates. In addition to demonstrating unique reactivities for the different classes of adsorbates, these studies revealed substrate-dependent reactivities. From a tribological perspective, we demonstrated the inherent difference in the frictional properties of stoichiometric TiC, VC, and titanium nitride with atomic force microscopy in both ambient and vacuum environments, thus allowing for the future design of advanced tribological counterfaces.

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Original Objectives

We propose to perform a comparative study of the surface chemistries of TiC, TiN, and VC. This work will focus on single crystal surfaces, first comparing the non-polar (100) crystal faces of these rock-salt structure materials, and progress to other crystal faces, such as the more reactive (111) surface. We propose to examine the effects of changing either the non-metal component (TiC vs. TiN) or the metal component (TiC vs. VC) on the surface bonding and reactivity of small molecules. The gas molecules that we plan to study possess a range of different chemical functionalities that should help distinguish the activity of the substrates and model functional groups found in spacecraft liquid lubricants and boundary additives, which are surface active species. The molecules under consideration include oxygen, water, ammonia, and methanol, to examine differences in electron donating, accepting, and deprotonation capabilities of the materials. We also propose to study trifluoroethanol and perfluoro-1,2-diethoxyethane as a model for PFPE lubricants, a chlorine containing molecule such as ethyl chloride as a model of boundary additives containing Cl, and triethylphosphate as a low molecular weight analog to tricresylphosphate, a widely used boundary additive in spacecraft lubrication. The interactions of the selected species with thin film coatings as a function of varying surface composition and crystallographic orientation will also be investigated to determine the relevance of the single crystal studies on the chemistry of real materials.

In conjunction with the studies of surface chemistry, comparative studies of the tribological properties of TiC, TiN, and VC are proposed. These studies will seek to develop a fundamental understanding of the tribology of these carbide and nitride materials by a combined use of ultra-high vacuum (UHV) atomic force microscopy (AFM) and surface analysis. It is well recognized that the friction and wear properties of most materials depend heavily on the physical and chemical nature of the contacting interface. Tribological measurements are easily influenced by surface roughness,⁴¹ surface cleanliness (absence of lubricating interfacial layer),⁴² and ambient environment,⁴³ as well as the elemental composition of the two contacting surfaces.⁴² To reach a fundamental understanding of a material's tribological properties, each of these variables must be carefully controlled or measured. The proposed UHV atomic force microscopy/ surface analysis studies will provide a unique opportunity to systematically measure all of the variables contributing to the behavior of a tribological contact. UHV AFM experiments will allow: (1) precise control over the environment surrounding the tribological contact, (2) the

unique opportunity to correlate tribological measurements with the exact chemical nature of the surface, and (3) the opportunity to specifically prepare model tribological interfaces of known composition and structure. The UHV AFM tribology studies performed at the University of Houston will rely heavily upon the information generated by the surface chemistry studies at Aerospace in preparing the carbide and nitride surfaces.

Status of Effort

Work on the contract # F49620-97-0029 was completed by 1/15/2000 (an approved extension of the contract into January of 2000 was approved by AFOSR). The accomplishments of this program are described in the sections that follow. During this reporting period, the research teams at the University of Houston and The Aerospace Corporation investigated the surface chemical interaction of a number of molecular adsorbates with the (100) face of titanium carbide (TiC) and vanadium carbide (VC) using an array of surface analytical measurement tools. Adsorbates included oxygen and water, considered important from an environmental "aging" perspective, carbon monoxide and ammonia as probes of the electronic structure model developed within this program, and a series of alcohols including methanol, ethanol, trifluoroethanol, isopropanol, and methyl allyl alcohol as probes of interfacial reactivity. An array of surface analytical techniques producing independent yet complimentary data were employed to develop a complete chemical and structural picture of the adsorption and reaction of these molecular adsorbates. In addition to demonstrating unique reactivities for the different classes of adsorbates, these studies revealed substrate-dependent reactivities. From a tribological perspective, we demonstrated the inherent difference in the frictional properties of stoichiometric TiC, VC, and titanium nitride (TiN) with atomic force microscopy (AFM) in both ambient and vacuum environments, thus allowing for the future design of advanced tribological counterfaces.

During the course of this contract, six peer-reviewed publications and one invited contribution to the *MRS Bullentin* have resulted from the funded work. Furthermore, the results and findings of this program have been the subject of 22 technical presentations made at national meetings, universities, and national and international laboratories.

Accomplishments/New Findings

The accomplishments of this program encompass studies of fundamental chemical and tribological phenomena that can be extended to practical systems. The surface chemical studies of the materials have employed small molecules of seemingly little tribological importance to gain a detailed understanding of surface chemical bonding phenomena and larger molecules that are more difficult to fully characterize but have a more direct link to lubricants and additives. Similarly, the tribological studies have been conducted on the fundamental level with atomic force microscopy and we have begun to extend our studies to a more practical level by using a pin-on-disk tribometer housed in an ultrahigh vacuum chamber. Our results will be presented to highlight the meaning of the results on both of these levels.

Interfacial Reactivity of Oxygen

The surface reactivity of these materials with oxygen has been investigated with XPS and HREELS. HREELS experiments were performed at both low temperatures (140 to 150K) and at room temperature, while XPS was performed at room temperature. These experiments have provided the first complete chemical identification of the surface reaction products of oxygen with the carbides, providing more direct evidence for the different chemical reactivity of these materials than had been available from previous ion scattering studies. Oxygen adsorbed dissociatively on both TiC and VC at all temperatures studied. The HREELS studies showed that the predominant surface reaction product on VC was an oxygen atom bound to a single vanadium species at an on-top site, with a stretching frequency of 970 cm^{-1} . This result was confirmed by XPS, which clearly showed a small perturbation of the V 2p core levels after exposure to oxygen, while the C 1s level remained unchanged, showing that oxygen interacts only with the metal atom under these conditions (exposures up to 300L). In contrast, the reaction of oxygen with TiC produced a small amount of oxygen adsorbed at the Ti on-top site at low exposures, with the majority of oxygen bound in multiple atom sites identified by a large lower frequency loss feature near 700 cm^{-1} . Our XPS results confirm that oxygen is interacting with both Ti and C atoms on the TiC surface, with the higher exposures showing clear evidence of higher oxidation states of titanium consistent with the onset of TiO_x formation enabled by the loss of carbon oxides. We have also identified a surface reaction intermediate on TiC that was

never observed on VC, a bound carbon monoxide molecule with an HREELS stretching frequency of 2000 cm^{-1} . Taken in total, these experiments have clearly demonstrated that TiC and VC have distinctly different reaction pathways with oxygen, where the TiC surface becomes oxidized because oxygen reacts with surface carbon, while a strong V=O surface species prevents significant oxidation of VC at these low exposures. As expressed in our program goals, we believe that this different surface chemistry is a direct outgrowth of the differing surface electronic structure of the two materials. The highest occupied energy levels on TiC are predominantly based on the C atom, making C the preferred adsorption site for the electrophilic O atoms and initiating the surface oxidation. The additional electron present in VC is located on the V atom, making it the preferred adsorption site and the formation of a very stable V=O species precludes the loss of carbon. We believe that the minor species observed in the HREELS data on both surfaces are the result of oxygen adsorption on defect sites.

Interfacial Reactivity of Water

Detailed study of the interaction of water with TiC(100) and VC (100) has provided the first complete chemical identification of surface reaction products, clarifying the different chemical reactivities of these materials. In this work, HREELS investigation of the surface chemical composition at a variety of temperatures and exposures were correlated with TPD and XPS experiments. Isotopic substitution (D_2O) was used in vibrational and desorption studies to aid in the identification of specific vibrational modes and distinguish desorbing species from background adsorbates. We have found that water adsorbed molecularly and dissociatively on both surfaces, but the relative quantities differed across the range of temperatures studied. On TiC, the decomposition of water proceeded at low temperature ($-130\text{ }^\circ\text{C}$), forming large amounts of surface hydride (with a characteristic vibrational frequency of 980 cm^{-1}) and hydroxyl (3650 cm^{-1}) species. As temperature increased, this reaction was followed by evolution of reaction products including H_2O , CO, CO_2 , and eventually H_2 as shown by TPD. In contrast, higher temperature ($-70\text{ }^\circ\text{C}$) was required to drive the reaction on VC, producing vibrational features indicative of decomposition (including surface hydride) and the evolution of H_2O , and H_2 . In this way, TPD has been used to help distinguish molecular from dissociative adsorption. XPS has also been used to quantify the relative amounts of chemical constituents of the adsorbed layer. Differences in the chemical behavior of the two substrates are marked by the greater

participation of the C atom in the chemistry of TiC, as we have seen previously with the interaction of oxygen. The predominantly C 2p character of the highest occupied molecular orbital on TiC results in surface electron donation from the carbon. However, since there are no occupied anti-bonding levels in the TiC electronic structure, the interaction with O or OH withdraws Ti-C bonding electron density and weakens the bond. The highest occupied levels in VC are the V 3d based anti-bonding molecular orbitals. The withdrawal of electron density upon adsorption of O or OH from these levels results in the formation of very stable V-O species and potentially strengthens the V-C substrate bonds. These measurements have also demonstrated the presence of greater quantities of hydroxyl species (a dissociation product of water) on TiC at cryogenic temperatures. These studies also reveal the relatively greater retention of oxygen containing moieties on TiC with increasing surface temperature. At room temperature, although all water has desorbed, the presence of a vanadyl (V=O) species is observed on VC, akin to the reaction product from the adsorption of molecular oxygen on VC. This result highlights the potential importance of this species in reaction pathways involving oxygen containing molecules adsorbed on VC.

Small Molecule Interactions – CO and NH₃

Carbon monoxide and ammonia were chosen for study as they have been widely used in the surface science community to investigate surface bonding phenomena. Specifically, CO can bond with a surface through a combination of σ -donor and π -acceptor interactions, while NH₃ adsorbs molecularly exclusively as a σ -donor. Any significant difference in the strength of the surface interaction based on the relative abilities of TiC and VC to donate or accept electrons is thus probed. This fundamental behavior is expected to influence the interaction of more complex molecules, lubricants and additives, with these materials and the studies performed with CO and NH₃ have been designed to more fully elucidate these interactions.

We have studied the interaction of CO with TiC and VC (100) using a range of techniques, including TPD, HREELS, XPS, and UPS. These experiments have clearly shown that CO adsorbs more strongly to VC than to TiC. Furthermore, the spectroscopic probes have clearly demonstrated that this enhanced bonding is the result of much stronger π -backbonding on the VC (100) surface relative to TiC. Specifically, the TPD results show that CO desorbs from VC at higher temperatures (with first order kinetics) than it does from TiC, where zero order

kinetics are observed. The HREELS results provide clear evidence for the enhanced backbonding on VC, as the C-O stretching frequency decreases to 2060 cm^{-1} from the gas phase value of 2143 cm^{-1} , consistent with donation into the $\text{CO } 2\pi^*$ level. On TiC, we observe very little CO adsorption under our experimental conditions, and the stretching frequency of reversibly adsorbed CO is 2120 cm^{-1} , demonstrating much less backbonding than is present on VC. The XPS results are consistent with this picture, as demonstrated in the C 1s and O 1s core level CO spectra that have satellite peaks related to final state effects in the photoemission process. Previous studies of CO adsorption on different materials with a range of interaction strengths (Ni, Ag, CuCl, ZnO) have demonstrated that the intensity of the satellite feature in the C 1s and O 1s regions relative to the expected core level feature can be related to the strength of interaction. The results obtained in our studies of CO adsorbed on VC and TiC indicate an intermediate degree of interaction of molecules in the first monolayer (the presence of π -backbonding), however with intensity ratios revealing more π -backbonding on the VC surface. This observation is in direct agreement with the greater red shift of the CO stretching frequency when adsorbed on VC, also associated with a backbonding mechanism.

The enhanced tendency for π -backbonding on VC is a direct result of the difference in the electronic structure of the two materials. Since TiC and VC have identical geometric structures, the only difference in their electronic structures arises from the extra electron present per formula unit of the VC. This electron resides in an orbital that is predominantly V 3d in nature (we believe essentially $3d_{xz, yz}$) having a perfect orientation for backbonding with the $\text{CO } 2\pi^*$. Alternatively, the highest occupied level in TiC is a C 2p based level, and no orbitals that are predominantly Ti 3d are occupied, essentially precluding backbonding. Therefore, any surface bonding or reaction that is influenced by the presence of electrons in these orbitals will be different on VC and TiC, and this is borne out in our CO results. Alternatively, the interaction of a σ -donating species should be little influenced by this electronic structure difference, and this is being probed through ammonia adsorption as described below.

Ammonia bonds molecularly to surfaces via the σ -donation of electrons from the $3a_1$ molecular orbital into an empty orbital. With both VC and TiC, the most reasonable interaction would be with a combination of metal $3d_z^2$, 4s, and $4p_z$ based orbitals, which are all essentially empty on both materials. Therefore, one would expect little difference in the manner in which NH_3 adsorbs on TiC and VC. Thus far, we have only probed this interaction with HREELS

studies of NH_3 adsorption at a variety of temperatures. Qualitatively, the two surfaces have very similar interactions with NH_3 . Under comparable conditions, the NH_3 loss features have similar intensities on the two surfaces, and appear at similar energies and show comparable shifts with decreasing coverage. Both surfaces lose NH_3 with increasing temperature, retaining similar amounts at 0°C . We await more data to quantify the interactions, but the surfaces appear to be coordinating NH_3 in very similar ways, consistent with the σ -donor interaction being comparable on the two surfaces.

Larger Molecules – Alcohols

To model the interaction of simple hydrocarbon and fluorocarbon lubricants and additives with metal-carbide surfaces, we have studied methanol (MeOH), ethanol (EtOH), isopropanol (IPA), methyl allyl alcohol (MAA) and trifluoroethanol (TFE) at a variety of temperatures and exposures. The OH terminal group on these molecules was chosen to enhance adsorption from the gas in UHV, since the sticking probability of the nonpolar alkane is very low, and to provide insight into oxygen containing basestocks and additives. With the number of adsorbates and the array of experimental techniques, the entire matrix of experimental results is not yet complete for every adsorbate. However, the results described in the following paragraphs continue to indicate rich and unique surface chemistries of TiC and VC toward these materials.

HREELS shows that these molecules (MeOH , EtOH , and TFE) adsorb similarly to both surfaces by forming methoxy, ethoxy, or trifluoroethoxy groups at -120°C . These surface states are each characterized by a metal-oxygen vibration at approximately 350 cm^{-1} , demonstrating that the adsorbate bonds to the surface metal atom. The C-O vibration is found at 1050 cm^{-1} (MeOH and EtOH) and 1100 cm^{-1} (TFE). Different reactivities between the two substrates, and between the various adsorbates, are found when comparing the relative intensities of the spectral features, and different reaction products result from increasing temperature.

In the case of methanol at low temperature (-120°C), we find that the ratio of intensities of the methyl asymmetric C-H stretch to the C-O stretch is greater when adsorbed to VC than to TiC. Since the dipole moment of the asymmetric methyl stretch is oriented perpendicular to the C-O bond, we conclude that the C-O bond is directed more normal to the TiC surface than to the VC surface. As the temperature was increased beyond -65°C , the C-O vibration shifted to 1130 cm^{-1} on VC, but remained at 1050 cm^{-1} on TiC. This shift in frequency corresponds to the

evolution of reaction products in the TPD spectrum which shows little reactivity with TiC, but a complex series of products on VC including formaldehyde, water, and hydrogen. Additionally, XPS of MeOH on VC showed a shift in the C(1s) feature as the methoxy group changed its chemical configuration. XPS measurements of methanol adsorbed on TiC are presently underway.

With ethanol exposures, the large intensity of the asymmetric C-H vibration in the HREELS spectra indicates that the C-C bond is oriented away from the surface normal on VC. With increasing temperature on the VC surface, the C-O bond again shifted to approximately 1130cm^{-1} at -75°C . At this temperature, the TPD spectra showed production of desorption products including molecular ethanol and the decomposition products of water and ethene. The propensity of the VC surface to selectively dehydrogenate alcohols has been investigated with TPD through the adsorption studies of isopropanol, trifluoroethanol, and methyl allyl alcohol. Similar to the case of ethanol, isopropanol undergoes dehydrogenation in a similar temperature regime with the predominant reaction product of propene. The strength of the VC surface in opening this selective reaction channel is demonstrated in the observation of difluoroethene as a reaction product of trifluoroethanol with VC. The electron withdrawing fluorine atoms would typically be associated with a lesser reactivity of the alcohol species, however reactivity similar to ethanol is again observed. Finally, TPD was used to study the adsorption of methyl allyl alcohol (2-methyl-2-propene-1-ol) on VC. Unlike the other alcohol species studied, the molecule does not possess hydrogen in the β site with respect to the hydroxyl functionality. This appears to be a critical step in the observed reaction mechanism (β hydride elimination) as MAA was observed to reversibly adsorb with little reactivity with the VC surface.

The HREELS spectrum of trifluoroethanol on TiC showed a clear C-C vibrational feature at 850cm^{-1} , while this peak was absent from the spectrum of TFE on VC. Furthermore, as observed with the alcohols above, the relative intensity of the asymmetric C-F stretching vibration was much larger on VC than on TiC. This indicates that the C-C dipole is preferentially oriented closer to the surface normal on TiC than on VC. We were unable to observe the shift in the C-O frequency with increasing temperature, since this feature could not be reliably resolved from the C-F stretching vibration. Still, as described above, the TPD spectra indicated an array of products, which resulted from the interaction of TFE with VC.

The results of the studies performed with a series of alcohols highlight the importance of potential reaction channels of carbide surfaces with lubricants. In summary, the most important findings of this study are: (1) the presence of an alcohol functionality enhances the bonding of hydrocarbon molecules to these substrates, (2) the formation of alkoxy species are observed at cryogenic temperatures on both VC and TiC, and (3) a selective dehydrogenation channel of reactivity producing alkenes from the parent alcohol at temperatures just above room temperature has been identified on VC. Many lubricants and additives contain oxygen containing functionalities and reactions as those observed in these studies may potentially influence the performance of both lubricants and additives through similar pathways.

Tribological Studies – AFM Results

The frictional properties of TiC(100), VC(100), and an epitaxial film of TiN(100) grown on MgO(100) were also investigated under ambient conditions. For these studies, the frictional response from a silicon nitride (oxynitride) sliding against the native oxides of these materials was measured under dry ambient conditions as well as a function of relative humidity. Under dry conditions, the coefficients of friction of VC and TiN are ~50% higher than that of TiC. As the humidity level is increased, an increase in the coefficient of friction by 33% is measured for TiC while 75% and 95% increases are observed for VC and TiN, respectively. These changes are fully reversible and suggest that the frictional increases arise from the physical adsorption of water at the model microasperity contact and not from surface chemical reactions. The magnitude of such changes in frictional properties with changes in relative humidity underscore the importance of a fundamental understanding of the frictional properties of these materials.

The frictional properties of single crystal titanium carbide (TiC), titanium nitride (TiN) and vanadium carbide (VC) were studied by atomic force microscopy (AFM). In this work, friction measurements were performed under controlled ambient conditions to emulate the introduction of these materials as hard coatings in terrestrial applications. Surface compositions of both clean and oxidized (air exposed) samples were characterized by XPS. To probe the frictional properties at various interfaces TiC, TiN and W₂C coated tips were used in addition to Si₃N₄ tip. The results of these studies lead to the following general conclusions. The friction coefficient of TiC was measured to be lower than those of TiN and VC in all cases. The coefficients of friction of TiN and VC were indistinguishable when friction was measured with a

Si₃N₄ probe tip; however subsequent investigations with conducting carbide and nitride coated tips clearly distinguished frictional differences between the two materials. The general behavior of these contacts can be summarized by the rule: interfaces of similar materials (carbide against carbide vs. carbide versus nitride) result in higher frictional properties. Comparative friction studies are currently being performed in vacuum environment to elucidate these differences. In light of the electronic model being developed to describe the surface chemical reactivity of these materials and the evidence for frictional energy dissipation via an electronic mechanism on vanadium carbide, it is possible that these materials are being distinguished tribologically through electronic differences. These studies have been partially enabled through work at The Aerospace Corporation to deposit thin films of titanium carbide on silicon nitride cantilevers. These efforts have also entailed spectroscopic investigation of the thin film deposits using HREELS and XPS to evaluate their surface composition and chemistry.

Atomic force microscopy (AFM) has been employed in an ultrahigh vacuum (UHV) environment to measure the frictional properties of single crystal vanadium carbide (VC) as a function of reaction with oxygen. The VC(100) surface, prepared by sputtering and annealing in vacuum, was found to be free of oxygen and to exhibit good crystallographic order with atomically flat terraces ~100-200 Å in width. The coefficient of friction between a silicon nitride probe tip and the clean VC surface was measured as 0.52 ± 0.04 . Chemical modification of this surface was accomplished by exposure to molecular oxygen that produced a saturation coverage of chemisorbed atomic oxygen. The coefficient of friction between the same silicon nitride tip and the “oxidized” VC surface in the wearless regime was measured as 0.32 ± 0.05 , representing an ~ 40 % reduction in friction. This reduction in friction is associated with a reduction in the density of metal *d* electrons nearest the Fermi level that occurs upon oxygen adsorption. The model adopted in this understanding is that energy is dissipated through the excitation of electron hole pairs at the interface- by reducing the density of electrons available for excitation, channels for energy dissipation are removed thereby reducing interfacial friction. These observations provide the first evidence for the contribution of an electronic mechanism of energy dissipation at the sliding interface of a solid-solid point contact.

The UHV studies of the frictional properties of the metal carbide surfaces have been extended to address the influence of the adsorption of additional interfacial species. Namely, the frictional properties of VC(100) have been probed with UHV AFM as a function of ethanol

exposure at room temperature. From the surface chemical studies described in the previous section, we understand that ethanol undergoes dehydrogenation and produces a bound surface species (most likely hydrogen deficient) stable at room temperature. Between 0 and 1000 L of ethanol exposure, the frictional response of VC is reduced by a factor of two in a monotonic fashion. This decrease is accompanied by a similar decrease in the pull-off force between the probe tip and the surface. These results are in direct contrast to the friction reduction observed upon exposure to molecular oxygen where the reduction in friction (in the absence of a change in adhesion) has been related to a change in the interfacial electronic structure. Instead in the case of ethanol adsorption, we believe that the shear strength of the interface is being directly modified through the incorporation of a hydrocarbon species into the sliding interface. More studies, at a variety of surface temperatures, and other longer chain alcohols and hydrocarbons will be performed in the near future to more fully elucidate this class of tribological modification.

Tribological Studies – UHV Tribometer

The UHV tribometer used in this work has a ball-on-flat geometry, with orthogonal strain gages mounted on flexures on the arm holding the ball. These orthogonal gages simultaneously measure the applied load and frictional forces measured during motion. The tribometer is housed in an ion-pumped vacuum chamber, and the pressure of the system during operation is 1×10^{-9} Torr. Both the ball and flat are exchangeable under vacuum conditions, such that samples can be cleaned and tested under UHV conditions, and then transferred to our small spot XPS facility where the wear spot on the ball and the track on the flat can be analyzed. In work applicable to this program, we have used Si_3N_4 balls (Norton NBD 200 material) and TiC-coated 440C balls (CSEM) in a variety of tests under UHV conditions. We've primarily determined the friction coefficient of these materials against 440C and 52100 bearing steels, although we have plans to extend the work to examine TiC, TiN, and VC-coated steel flats in our follow-on proposal. This work is aimed to emulate the AFM studies described above, but on a macroscopic scale using real engineering materials. The Si_3N_4 ball is the engineering equivalent to the Si_3N_4 AFM tips used in some of our work. The goal is to demonstrate how the events studied on the microscopic level scale to the macroscopic level.

Fairly low friction coefficients have been reported for these material combinations in unlubricated sliding in air. For example, the friction coefficient reported for TiC sliding against 440C in air has ranged from 0.1 to 0.2, which is low enough to consider using these materials without lubrication. However, our results in UHV have produced average dynamic friction coefficients in the range of 0.4 to 0.5 for this combination, levels that are unacceptably high and somewhat erratic. The value of effective lubrication and boundary additives for these systems to lower the friction is quite clear, particularly for vacuum applications as commonly encountered in spacecraft mechanisms.

Significance to the Field

The work being performed under this contract directly impacts a number of research fields through its fundamental approach. This study impacts the field of hard coatings technology by performing experiments on model single crystal compounds in an effort to provide a basic understanding of their surface chemical reactivity. Both TiC and TiN can be found as tribological coatings in current applications and are being considered as potential tribological materials in the newly emerging field of microelectromechanical systems (MEMS). The studies being performed under this research contract are providing the framework for understanding the interfacial reactivity of such materials. This study has been significant to the tribological community through the fundamental UHV-AFM experiments being developed and performed which are correlating frictional properties with an exact knowledge of the surface chemical composition. Furthermore, the study of these carbide and nitride materials has allowed a fundamental assessment of the mechanisms of energy dissipation at this sliding interface and illustrated a unique channel of energy dissipation. Finally, this project has impacted the general field of surface science through its exploration of *compound* single crystal materials. Our work serves as a model of the approach using complementary techniques that must be adopted for a complete understanding of the complex interactions that may occur on multi-component systems.

Relationship to Original Goals

The research progress described in this report directly addresses the goals outlined in the original proposal focussing on the fundamental chemical and tribological behavior of metal carbide and metal nitride materials. The work described herein also provides the basis for the

additional studies in the areas of lubricant reactivity on the single crystal surfaces and thin film behavior (friction, wear, and reactivity) of these materials. Lubricant reactivity studies are currently underway and funded through an additional AFOSR contract. Activities involving the development of new experimental capabilities, funded through AF-DURIP programs and internally at The Aerospace Corporation, have been largely successful and are directly contributing to the progress being made in our ongoing studies. The original goals of this project also included proposed studies on TiN and polycrystalline carbide substrates. We were unable during this period to obtain suitable substrates of these materials for our studies, however our present contract includes work to this end.

Relevance to Air Force Mission

Advanced anti-wear materials, such as hard-coated components, are beginning to find use within Air Force, DoD, and NASA spacecraft systems. Specifically, TiC-coated bearing balls are used in the filter wheel mechanisms in the NASA/GOES spacecraft and in the reaction wheels of the NASA/AXAF (Chandra) telescope. These same materials were baselined for the reaction wheels of the SBIRS-Low FDS program. In our experience, even though the hard coatings are improving performance, several questions still remain that require a fundamental understanding of the surface chemistry and tribology of these materials. In general, the same lubricants and that have been used with steel components are being used with hard coatings, with little or no insight into chemical incompatibilities or optimization of formulations. For example, the PFPE lubricant used in one of these applications appeared to chemically react with and create pits on the TiC-coated ball, making a detailed understanding of the chemical interaction of fluorocarbon species with TiC highly desirable. With our work, we seek to provide a fundamental perspective to enable these decisions to be made based on scientific principles.

Our work under this contract represents the first comprehensive study attempting to uncover the detailed surface chemical properties of commercially relevant hard coating materials and to relate this chemistry to tribological performance. To date, our studies have explored how a number of model chemical species (oxygen, water, carbon monoxide, ammonia, and a series of short chain alcohols) interact with TiC and VC (100) surfaces. These studies lay the groundwork for understanding the reaction of these carbide materials with lubricants and boundary additives used in space applications. Boundary additives are used to limit friction and wear in mechanical

contacts by bonding to, and reacting with, mechanical components. Many of these additives contain oxygen atoms that are the surface active species. Our studies are defining how these additives will react with hard coating materials. Our work has shown that the function of such additives with these materials will likely depend on the Lewis base properties of the oxygen sites, their potential for chemical reactions resulting in electron withdrawal from the surface, and specifics of the electronic structure of the carbide surface. We will soon expand our work to study analogs of spacecraft lubricants based on our developing understanding of the chemical properties of the materials. In addition, we will conduct similar TPD and XPS experiments on polycrystalline thin films (when those substrates become available) to correlate engineering materials to our single crystal studies.

The AFM surface friction studies are providing unique and critical insight into the relationships between surface chemistry and tribology. In particular, the friction and lubrication of hard coating materials under ultra high vacuum conditions is critical from a fundamental perspective of completely controlling the tribological system both physically and chemically. Of equal importance, we are quantifying the performance of these materials in environments that mimic those of space applications. This work will enable us to define better under what circumstance, if any, these materials can be used in unlubricated contacts. These studies will further help to define the next generation of spacecraft lubricants that will be required to ensure that hard coatings can achieve their potential for extending spacecraft mission life and performance.

Potential Applications to Air Force and Civilian Technology Challenges

The operation of spacecraft moving mechanical assemblies has been a technological challenge since the inception of the space program. The key to enhancing the reliability and operational lifetimes of such systems is the control and reduction of friction and wear at mechanical interfaces. Hard coatings have the potential to enhance greatly the tribological properties of mechanical systems by reducing wear and altering lubricant breakdown pathways that are inherent in steel systems. This research program is currently focusing on fundamental surface chemical and tribological phenomena that we believe will inevitably feed into technology development programs. In the final year of our work, we will be correlating our results to friction and wear studies conducted on hard coated mechanical components, assessing the

performance of various materials and lubricant combinations. Our results will have a direct impact on Air Force, DOD, NASA, and commercial space programs as all spacecraft have critical mechanical assemblies; the knowledge gained will be generic and broadly applicable.

Spacecraft mechanisms that will likely be impacted include both relatively slow speed and high-speed devices. For example, scanning devices that operate under boundary lubrication conditions and typically house mission critical sensors and antennas will benefit from wear reduction and lower friction potentially offered by hard coatings. High speed devices such as momentum wheels may benefit from altered lubricant degradation pathways provided by hard coatings. Variable speed reaction wheels must operate under a wide range of tribological conditions, and properly applied hard coating technology will provide greater flexibility for these devices. In short, every mechanical system will benefit from reductions in friction and wear. Our program is providing fundamental insight into the nature of these phenomena for hard coating materials, and we plan to extend our work into applied studies as our knowledge grows.

Personnel Supported During the Course of the Contract

Dr. Scott S. Perry (University of Houston)

Dr. Philip Merrill (University of Houston)

Hyun I. Kim (University of Houston)

Oussama El-Bjeirami (University of Houston)

Rebecca Guenard (University of Houston)

Luis Fernandez (University of Houston)

Dr. Steve Didziulis (The Aerospace Corporation)

Dr. Peter Frantz (The Aerospace Corporation)

Dr. Gouri Radhakrishnan (The Aerospace Corporation)

Publications

(published or submitted during the period December 1996- December 1999)

Peter Frantz, Stephen V. Didziulis, Philip B. Merrill, Scott S. Perry, *Spectroscopic and Scanning Probe Studies of the Interaction of Oxygen and Water with TiC and VC (100) Surfaces*, Tribology Letters, **4** (1998).

Judith A. Harrison and Scott S. Perry, *Friction in the Presence of Chemical and Hard Coatings*, MRS Bulletin, **23**(6) (1998) 27.

Peter Frantz and Stephen V. Didziulis, "Detailed Spectroscopic Studies of Oxygen on Metal Carbide Surfaces", Surface Science, **412/413** (1998) 384-396.

Philip B. Merrill, Scott S. Perry, Peter Frantz and Stephen V. Didziulis, *Adsorption of Water on TiC(100): Evidence for Complex Reaction and Desorption Pathways*, J. Phys. Chem., **102** (1998) 7606-7612.

Philip B. Merrill and Scott S. Perry, *Fundamental measurements of the friction of clean and oxygen-covered VC(100) with ultrahigh vacuum atomic force microscopy: Evidence for electronic contributions to interfacial friction*, Surface Science, **418** (1998) 342-351.

Stephen V. Didziulis, Peter Frantz, Scott S. Perry, Oussama El-bjeirami, Syed Imaduddin, and Philip B. Merrill, *Substrate-Dependent Reactivities of Water on Metal Carbide Surfaces*, J. Phys. Chem. B, **103**(50) (1999) 11129-11140.

Seungwhan Lee, Oussama El-bjeirami, Scott S. Perry, Stephen V. Didziulis, Peter Frantz, and Gouri Radhakrishnan, *The Frictional Properties of Titanium Carbide, Titanium Nitride, and Vanadium Carbide: Measurement of a Compositional Dependence with Atomic Force Microscopy*, J. Vac. Sci. Tech. **18**(1) (2000) 69-75.

Interactions/Transitions

a. Presentations:

- Dr. Didziulis spoke at the 1997 National Meeting of the American Vacuum Society in San Jose. The title of the presentation was "Detailed Spectroscopic and Scanning Probe Studies of Oxygen and Water on Metal Carbide Surfaces."
- Dr. Didziulis was an invited speaker at the 1997 National American Chemical Society Tribology Symposium.
- Dr. Scott Perry presented an *invited* talk at the International Conference on Metallurgical Coatings and Thin Films in San Diego, CA during the week of April 27, 1998. The title of his talk was "Fundamental Characterization of Carbide and Nitride coating materials: Correlation of Surface Composition and Frictional Properties."
- Dr P. Frantz presented a paper entitled "The Influence of Adsorbates on the Chemical and Tribological Properties of Metal Carbide (100) Surfaces" at the Tribology Symposium of the American Physical Society National Meeting in Los Angeles, March 22, 1998.
- Mr. Oussama El-Bjeirami presented a paper entitled "Adsorption of D₂O on TiC(100) and VC(100): A Comparative Surface Reactivity Study" at the Texas Surface Science Round-Up

Meeting held in May, 1998 in Round Top, Texas. (Dr. Perry is the founder and organizer of this surface science meeting which encourages student interaction and participation.)

- Dr. Scott Perry presented an *invited* talk at the Omicron West Coast Technical Conference held in San Francisco, CA on May 29, 1998. His presentation discussed the results of fundamental friction measurements on vanadium carbide surfaces and was entitled "Evidence for Frictional Energy Dissipation Via an Electronic Mechanism."
- S. S. Perry, "Atomic and Molecular Level Studies of Friction", University of Houston. Department of Mechanical Engineering, September 22, 1998
- S. S. Perry, "Experimental Evidence for Electronic Contributions to Interfacial Friction", American Vacuum Society National Symposium, Baltimore, MD, November 5, 1998
- S. S. Perry, "Novel Channels of Chemical Reactivity at Transition Metal Carbide Surfaces" Georgia Institute of Technology, Atlanta, GA, January 14, 1999
- S. S. Perry, "Novel Channels of Chemical Reactivity at Transition Metal Carbide Surfaces" Mesilla Conference on Interfacial Science, Mesilla, NM, February 9, 1999
- S. S. Perry, "Novel Channels of Chemical Reactivity at Transition Metal Carbide Surfaces" (Poster presentation), Gordon Conference- Chemical Reactions at Surfaces, Ventura, CA, March 2, 1999
- S. S. Perry, "Novel Channels of Chemical Reactivity at Transition Metal Carbide Surfaces" Northwestern University, Surface Science Colloquium, Evanston, IL, March 12, 1999
- S. S. Perry, "Novel Channels of Chemical Reactivity at Transition Metal Carbide Surfaces" University of Pittsburgh, Surface Science Colloquium, Pittsburgh, PA, March 15, 1999
- S. V. Didziulis, P. Frantz, G. Radhakrishnan, S. Lee, O. El-bjeirami, S. S. Perry, "Fundamental Chemical and Tribological Studies of Transition Metal Carbides," ACS National Meeting, Anaheim, CA, 24 March 1999.
- S. S. Perry, S. V. Didziulis, P. Frantz, G. Radhakrishnan, S. Lee, and O. El-bjeirami, "The Surface Chemistry and Tribology of Transition Metal Carbides and Nitrides", Wright Patterson Air Force Base, Dayton, OH, March 29 1999.
- S. S. Perry, "Fundamental Studies of the Frictional Properties of Metal Carbide Hard Coatings" American Vacuum Society International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 12, 1999
- S. S. Perry, "Novel Channels of Chemical Reactivity at Transition Metal Carbide Surfaces" Lawrence Berkeley National Laboratory, Surface Science Colloquium, Berkeley, CA, May 6, 1999

- R. Guenard, O. El-bjeirami, and S. S. Perry, "The reactivity of Small Alcohols on VC(100)", Texas Surface Science Round-up, Winedale, TX. May 26, 1999
- S. S. Perry and S. V. Didziulis, "The Surface Chemistry and Tribology of Transition Metal Carbides and Nitrides", AFOSR/ONR/NSF Tribology Program Review. Islamorada, FL, June 16, 1999
- S. S. Perry, "The Surface Chemistry and Tribology of Transition Metal Carbides and Nitrides", Swiss Federal Institute of Technology, Zurich, Switzerland, August 12, 1999
- Dr. Perry presented a poster entitled "The Surface Chemistry and Tribology of Transition Metal Carbides and Nitrides" at the Wright Patterson Air Force Laboratory, Materials Directorate Program Review in Dayton, OH on December 12, 1999.

b. *Consultative and Advisory Functions*

Dr. Perry visited the Materials and Manufacturing Directorate of the Air Force's Wright Laboratory in March of 1998 and reported on the most recent findings of the program. Dr. Perry consulted at this time regarding the properties of metal carbides and metal nitrides as well as recent advances in experimental approaches to measuring fundamental friction properties. Dr. Perry also participated in the Wright Patterson Air Force Laboratory, Materials Directorate Program Review in December of 1999 and provided an overview of the program accomplishments and the relationship between fundamental research being performed in a university setting and that being carried out at Wright Patterson.

The primary function of the Aerospace Corporation is to advise USAF/SMC and classified customers on matters related to the design and manufacture of spacecraft systems. Dr. Didziulis participates in numerous technology development programs that will directly benefit from the knowledge gained in this work. Aerospace provides a direct path for the insights gained in this research for implementation in current and future AF and DoD space systems. Dr. Didziulis consults on a regular basis with personnel from the Materials and Manufacturing Directorate at AFRL (Wright Laboratory). These personnel include J. Zabinski, C. E. Snyder, and L. Gshwender. Topics discussed in these meetings are the development of new spacecraft lubricants and the use of hard coatings on ball bearing surfaces. These interactions have occurred at Aerospace and at WL.

c. *Transitions*

While we have made no direct transition of information from this program, we strongly believe that we will make a significant contribution to the use of hard coatings in spacecraft systems. We have an active collaboration with WL investigating the lubrication of hard materials, we interact with satellite component manufacturers (e.g., Honeywell) that have numerous AF and DoD programs investigating the use of hard coated ball bearing components, and we work with NASA on reaction wheel systems that include hard-coated ball bearing components. This work will provide insight into the lubrication of these hard coated components when it is coupled to our ongoing work in support of these numerous programs.

New Discoveries

- A fundamental approach to the characterization of tribological properties has lead to the new discovery of electronic contributions to frictional properties of microasperity contacts of conducting materials. This discovery is currently being explored in order to assess the appropriate parameter by which tribological materials can be classified in terms of electronic friction.

Honors/Awards

Scott S. Perry (PI)
National Science Foundation CAREER Award, April 1999

Scott S. Perry (PI)
1997 University of Houston Cooper Award for Teaching Excellence